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EQUATIONS FOR VAPOR PRESSURES AND LATENT HEATS, INCLUDING APPROXIMATE EQUATIONS FOR SOLID COMPOUNDS CONTAINING A GASEOUS COMPONENT.*

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After early papers by Kirchoff[1] and Rankine[2] the subject of vapor pressure equations was thoroughly treated by Gibbs,[3] subject to the provisions that the vapor is an ideal gas of invariable specific heat, and the density and the specific heat at constant pressure of the liquid or solids are constant. Of the many vapor pressure equations that have been published we will mention here only that of Nernst,[4] which was applied to solids, and which assumes the vapor to be an ideal gas, and the specific heats to be functions of the temperature (usually in series expansion). Van der Waals and also van Laar have discussed the vapor pressure equation[5] in the light of the van der Waals equation of state.

An equation derived by Kirchoff and by Gibbs and discussed by Gibbs for either solids or liquids is

$$\log p = A - B \log T - C/T \qquad (1)$$

where A, B, and C are constants.

Keyes and Hara[6] found that $\log p$ is linear in $1/T$ for the silver-silver oxide equilibrium up to 388 atmospheres and pointed out that the equation deduced by Pollitzer from the previous measurements of Lewis, with the aid of the Nernst heat theorem in connection with series expansions of specific heats, failed to represent the data. The failure of the equation to serve as an interpolation formula for the range covered by the measurements of Lewis is evident: it may be that it is not due entirely to the series expansion of specific heats at very low temperatures, now known to be erroneous, but possibly in part due to failure to apply corrections to the ideal gas law. It has often been found that experimental data on decomposition pressures may be satisfactorily correlated when B in equation (1) is put equal to zero, which corresponds in the derivation of (1) to the assumption that the increase of heat capacity in the evaporation is zero, and it may be that there is some advantage in either keeping

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both the term $B \log T$ and the corrections to the ideal gas law or rejecting both together.

We shall here present the general vapor pressure equation, containing no assumptions beyond the two laws of thermodynamics, and then develop its application by means of simplifying assumptions, with especial reference to the decomposition pressures of solids.

2. Derivation of the General Vapor Pressure Equation.

Let us consider a system in two compartments, separated by a membrane which we may at will imagine as solid and impermeable, or freely permeable to gas. Let a solid and its compound with a gas, for example, $BaCl_2$ and $BaCl_2 \cdot 8NH_3$, be present in one compartment, filling it to the exclusion of any gas, and let the pure gas which may be evolved by the compound, for example, ammonia, be present alone in the other compartment. When the membrane is impermeable we may change the condition of the gas by changing independently the temperature T and the pressure p. The change of chemical potential of the gas μ will be given by

$$d\mu = -s\,dT + v\,dp \tag{2}$$

where s is the entropy and v the volume of a mole of the gas, by Gibbs' equation 97. It will be convenient to write a similar equation for the chemical potential of the gaseous component in the compartment containing nothing but the solids:

$$d\mu = -\bar{s}\,dT + \bar{v}\,dp \tag{3}$$

where $\bar{s}$ and $\bar{v}$ will refer to the gaseous component in the solids and may be called the partial molal entropy and the partial molal volume of the gaseous component in the solids. The next four paragraphs deal with the exactness of this.

The solids, considered collectively in this way as if they were a single phase, may be called the condensate. As already pointed out,[7] "the condensate has then a potential, a partial molal volume, etc., with respect to a given component, and the Gibbs theory applies to these quantities just as to the usual quantities distributed among the individual phases, the arguments not being changed." This was justified by the consideration that there is no logical necessity for always dividing up the extensive thermodynamic properties like the energy, the thermodynamic potential, the volume, etc., among the individual phases, but they may for special purposes be divided up,

one portion to the gas, and the rest to the condensed phases considered collectively. The reasoning, which was merely outlined, involves some difficulties, which will be avoided if we take advantage of Gibbs' equation 121.

The chemical equation for the formation of the compound may be written:

$$1/8\ BaCl_2 + NH_3 = 1/8\ BaCl_2 \cdot 8\ NH_3 \quad \text{(type reaction)} \qquad (4)$$

$$\nu S + G = \nu SG \quad \text{(general reaction)} \qquad (5)$$

where S represents the chemical symbol for the solid, G that for the gas, and SG that for the compound of solid with gas. Writing μ_S, μ, and μ_{SG} for the potentials of solid, gas, and compound, repectively, Gibbs' equation 121 becomes

$$\nu\mu_S + \mu = \nu\mu_{SG} \qquad (6)$$

Now each potential in equation (6) may be regarded as a function of the two variables T and p. We have by differentiation

$$(d\mu/dp)_T = \nu(d\mu_{SG}/dp)_T - (d\mu_S/dp)_T \qquad (7)$$

$$(d\mu/dp)_T = \nu(v_{SG} - v_S) \qquad (8)$$

where v_S and v_{SG} are the volume of a mole of solid and compound respectively. The last term in equation (8) is the increase in volume of the solids attending the reaction represented by equation (5). It may be regarded as the partial molal volume of the gaseous component in the condensate, since if V be the total volume of the condensate, n_1 the number of moles of gaseous component and n_2 the number of moles of solid S it contains, the partial volume of the gaseous component would be defined as $(\partial V/\partial n_1)$, where the variation is at constant T, p, and n_2, and by reason of equation (5) we should have

$$(\partial V/\partial n_1) = \nu(v_{SG} - v_S) \qquad (9)$$

This is therefore, by equation (8), the value of the quantity written in equation (3) as $\bar{v}$ for brevity, as the potential μ is the same regardless of the choice of the other components, as shown by Gibbs.

Similarly it may easily be seen that

$$(d\mu/dT)_p = -\nu(s_{SG} - s_S) = -\bar{s} \qquad (10)$$

It will be observed that the concept of the potential of ammonia

in a *compound* such as $BaCl_2 \cdot 8NH_3$ is inconvenient since the partial volume of ammonia in it is hardly a fit subject of discussion, as the composition of a chemical compound is not susceptible of the continuous variation indicated by $\partial E/\partial n_1$ or $\partial V/\partial n_1$. The partial volume of ammonia in the condensate is however physically interpretable through equation (9). The potential of ammonia in the condensate is interpretable through equation (6). The difficulty due to the law of definite proportions is similarly removed in the case of other partial thermodynamic quantities, such as heat capacity. Such considerations apply to the solids of any univariant system, and are useful when the system considered has a variance greater than one, provided the extra variance is due to the presence of other gases which are inert, not reacting with the solids.

We may now proceed to derive a vapor pressure equation from equations (2) and (3) by integration and elimination of the potentials. Since $d\mu$ is a perfect differential, the increase of potential $\Delta\mu$ of the gas in passing from a standard state defined by the values T_0 and p_0 to the variable state given by T and p may be found by integrating equation (2) along any path we please, and it is convenient to integrate first at the constant pressure p_0 to the values T, p_0, and then at constant temperature T to the values T, p. The state given by T_0 and p_0 is arbitrary, and will usually be taken at the lowest experimental temperature and vapor pressure under consideration. The variation of entropy at constant pressure is given by

$$(ds/dT)_p = C_p/T \tag{11}$$

Hence, if s_0 is the molal entropy of the gas at T_0, p_0, the entropy at T, p_0 is

$$s = \int_{T_0}^{T} C_p d \ln T + s_0 \tag{12}$$

where C_p is the constant pressure specific heat at p_0 and T. The increase of potential $\Delta\mu$ for the gas is therefore

$$\Delta\mu = -\int_{T_0}^{T}\left[\int_{T_0}^{T} C_p d \ln T + s_0\right] dT + \int_{p_0}^{p} (v - RT/p)\, dp + RT \ln (p/p_0) \tag{13}$$

Here we have added and subtracted the integral of $RT\, dp/p$ from the right-hand side in order to display the term $RT \ln p$, which occurs

in any vapor pressure equation as soon as a convenient equation of state is chosen.

For the solids,

$$\bar{s} = \nu(s_{SG} - s_S) = \int_{T_0}^{T} \nu(c_{SG} - c_S)\, d \ln T + \bar{s}_0 \qquad (14)$$

by equation (10) and the general equation (11) applied to each solid phase, where $\bar{s}_0$ is the difference $\nu(s_{SG} - s_S)$ at T_0, p_0. Let $\nu(c_{SG} - c_S)$ be represented by $\bar{c}$, which may be called the molal specific heat at constant pressure of the gaseous component in the condensate. Then the increase $\Delta\mu$ for the solids is

$$\Delta\mu = -\int_{T_0}^{T} \left[\int_{T_0}^{T} \bar{c}\, d \ln T + \bar{s}_0 \right] dT + \int_{p_0}^{p} \bar{v}\, dp \qquad (15)$$

Now along the vapor pressure curve μ is the same for both gas and solid and hence also $\Delta\mu$; furthermore, T and p are the same for both, including the particular values T_0 and p_0. Elimination of $\Delta\mu$ from equations (13) and (15) gives the vapor pressure equation:

$$RT \ln p = RT \ln p_0 + \int_{T_0}^{T} \int_{T_0}^{T} (C_p - \bar{c})\, d \ln T\, dT + (s_0 - \bar{s}_0)(T - T_0) - \int_{p_0}^{p} (v - RT/p - \bar{v})\, dp \qquad (16)$$

which may be transformed into

$$\ln p = \ln p_0 + \frac{1}{RT} \int_{T_0}^{T} \int_{T_0}^{T} (C_p - \bar{c})\, d \ln T\, dT + \frac{\lambda_0}{RT_0} - \frac{\lambda_0}{RT} - \frac{1}{RT} \int_{p_0}^{p} (v - RT/p - \bar{v})\, dp \qquad (17)$$

by virtue of the thermodynamic relation:

$$\lambda_0 = T_0 (s_0 - \bar{s}_0) \qquad (18)$$

where λ_0 is the latent heat of vaporization of 1 mole of the gaseous component at T_0, p_0. In these equations $(C_p - \bar{c})$ is for the constant pressure p_0, and $(v - RT/p - \bar{v})$ is for the temperature T, which is held constant for the last integration.

Equation (17) is the general vapor pressure equation. It is exact, depending only on the two laws of thermodynamics. It holds not only for solid compounds which evolve a gas, but also for liquids, if $\bar{c}$, $\bar{s}$, and $\bar{v}$ are understood to be the specific heat, the entropy and the volume of 1 mole of liquid.

3. Discussion of the Integrals.

The value of the single integral of equations (16) and (17) depends evidently on both T and p. But this integral proves to be of but small influence on the calculated value of ln p, compared with the influence of the term λ_0/RT, so that an approximate value of p serves to evaluate the integral closely enough to give a very good value of ln p. It is for this reason that the addition of a quantity equal to zero in obtaining equation (13) was significant.

The single integral of equation (17) may be discussed as regards the two parts $(v - RT/p)\,dp$ and $\bar{v}\,dp$. As regards the second, $\bar{v}$ is the volume of the gaseous component in the liquid or in the solids at the temperature T and the integration extends from p_0 to p, so that the condensed phase would from a physical standpoint be supersaturated with vapor all the way up to the upper limit of integration. Theoretically this is of no consequence, as a perfect differential $(d\mu)$ may be integrated along any path, irrespective of equilibrium conditions. Practically, the compressibility might be determined if necessary at higher pressures and extrapolated into the desired range with doubtless sufficient accuracy.

The integral of $(v - RT/p)\,dp$ may be calculated from the Beattie-Bridgeman equation of state in its original pressure form,[8] but this requires integration by parts, yielding functions of the volume which would necessitate solving the equation for the volume by the method of successive approximations.

Beattie[9] has given another form of the equation, the volume form, which is

$$v = RT/p + \beta/RT + \gamma p/R^2T^2 + \delta p^2/R^3T^3 \tag{19}$$

where

$$\left.\begin{aligned} \beta &= RTB_0 - A_0 - Rc/T^2 \\ \gamma &= -RTB_0b + A_0a - RB_0c/T^2 \\ \delta &= RB_0bc/T^2 \end{aligned}\right\} \tag{20}$$

which permits an easy integration of $(v - RT/p)\,dp$ in a series of powers of p:

$$\int_{p_0}^{p} (v - RT/p)\,dp = \frac{\beta}{RT}(p - p_0) + \frac{\gamma}{2R^2T^2}(p^2 - p_0^2) + \frac{\delta}{3R^3T^3}(p^3 - p_0^3) \tag{21}$$

Constants for 14 gases (including air) have been given for the pressure equation.[10] Constants for the volume equation have not yet been determined from the pressure data. Beattie has shown however[9] that constants as determined for the pressure equation may be used in the volume equation with good results for gases above their critical temperatures. The results were not so good for gases near the critical temperature and also near the saturation line, although they were considerably better than those obtained with the ideal gas law.

The double integral of equation (17) is a function of one variable T. If C_p and $\bar{c}$ are representable by a series expansion, which will usually be the case except at very low temperatures, an expression will hold such as

$$C_p - \bar{c} = \text{A} + \text{B}T + \text{C}T^2 + \text{D}T^3 \tag{22}$$

Substitution into the double integral J_2 of equation (17) and integration between the limits T_0 and T gives

$$J_2 = \text{A}T \ln T - \text{A}T_0 \ln T_0 - \left[\text{A} + \text{A} \ln T_0 + \text{B}T_0 + \frac{\text{C}T_0^2}{2} + \frac{\text{D}T_0^3}{3}\right](T - T_0) + \frac{\text{B}}{1\cdot 2}(T^2 - T_0^2) + \frac{\text{C}}{2\cdot 3}(T^3 - T_0^3) + \frac{\text{D}}{3\cdot 4}(T^4 - T_0^4) \tag{23}$$

4. Application of the Vapor Pressure Equation to Experimental Data

When the specific heats, volumes, and the latent heat are sufficiently known, equation (17) furnishes of course a test for the thermodynamic consistency of the data.

When only the specific heats and the volumes are sufficiently known, λ_0, the latent heat at T_0, p_0, can be found by plotting for instance $(\ln p - J_2/RT + J_1/RT)$, where J_1 indicates the single integral and J_2 the double integral of equation (17), against $(1/T_0 - 1/T)$, λ_0 being found from the slope of the best straight line. The constant p_0 will have been determined from a preliminary smoothing of the data.

The case of liquids has not been studied to determine to what degree simplification by approximation may safely be carried. In this case much is demanded of a vapor pressure equation, on account of the high precision attainable in the experimental measurement of the vapor pressure of liquids.

In the case of solids which evolve a gas, the relations are more favorable. The precision attainable in measurements of decomposition pressures is not so high as in the case of liquids, probably on account of strains in the solids, which are not quite of negligible thermodynamic effect. The decomposition pressure of solids at any temperature is always less than the normal vapor pressure of the liquid, and often much less. Thus there is less demand on the equation of state for the gas, and equation (21) will often suffice when the constants used are those determined for the pressure form of the equation of state. Other approximations will usually be permissible, and are made below.

The quantity $\bar{v}$ is known for many solids for a particular temperature and pressure. It does not vary much in a series of similar compounds, and when it is unknown for some compound, the value for a similar compound may be used. It may be considered a constant with respect to temperature and pressure changes.

As respects the specific heats, the quantity $(C_p - \bar{c})$ will at present have to be regarded as a constant, at least in most cases, and as an unknown adjustable constant in many cases, because of the lack of data for calculating $\bar{c}$.

It appears inadvisable to retain terms expressing variations of $\bar{v}$ or $\bar{c}$ unless these are known from independent data. If they are kept and treated as adjustable constants, a better representation of data may be expected, but the resulting equation is likely to represent errors which ought to be disregarded, and in such a case not only will these constants receive fictitious values, but the values found for the latent heat will suffer a loss of accuracy.

Treating $(C_p - \bar{c})$ and $\bar{v}$ as constants, and using the volume equation for the gas, the following approximate equation is easily obtained especially for decomposition pressures of solid compounds.

$$\log p = \log p_0 - \frac{M(C_p - \bar{c})}{R}\left(\frac{1}{M}\log\frac{T_0}{T} + 1 - \frac{T_0}{T}\right) + \frac{M\lambda_0}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right) + \frac{M}{RT}\left(\bar{v} - \frac{\beta}{RT}\right)(p - p_0) - M\gamma(p^2 - p_0^2)/2R^3T^3 - M\delta(p^3 - p_0^3)/3R^4T^4 \quad (24)$$

where β, γ, and δ are calculated from equations (20) for the given value of the variable temperature T, and M is the modulus of logarithms, 0.43429 . . , common logarithms being denoted by log.

If therefore we put

$$y = \frac{1}{1/T_0 - 1/T}\left[\log (p/p_0) - M\left(\bar{v} - \frac{\beta}{RT}\right)(p - p_0)/RT + M\gamma\,(p^2 - p_0^2)/2R^3T^3 + M\delta(p^3 - p_0^3)/3R^4T^4 \right. \quad (25)$$

and

$$x = \frac{1}{1/T_0 - 1/T}\left(\frac{1}{M}\log\frac{T_0}{T} + 1 - \frac{T_0}{T}\right) \quad (26)$$

a plot of y against x should give a straight line whose slope dy/dx is $-M(C_p - \bar{c})/R$ and whose intercept on the axis: $x = O$, is $M\lambda_0/R$. In this way the data can be treated when $(C_p - \bar{c})$ is unknown, and the constants be determined. The constant p_0 will have been found by a preliminary smoothing of the data, plotting log p against $1/T$. Points corresponding to values of T, p very close to T_0, p_0 may be found far off the line, and no attention need be paid to them in selecting the best line.

The constants $(C_p - \bar{c})$ and λ_0 having been determined, equation (24) may be used to calculate the decomposition pressure corresponding to the temperature T. The last three terms may be calculated by the use of an approximate value of p, as determined for instance by use of the preliminary plot or equation used for obtaining the value of p_0, and then corrected if necessary by the use of the improved value of p thus found. The convergence is rapid.

Equation (24) was applied in this way to the data of Gillespie and Lurie[11] on the decomposition pressures of the system

$$BaCl_2 + BaCl_2 \cdot 8NH_3,$$

which extend from 0° C. to about 50° and to about 9 atmospheres. No particular difficulty was encountered. In fact, the last two terms of equation (24) never exceeded 0.03 per cent of the pressure, a negligible matter in the case of an equilibrium involving solids. The quantity $\bar{c}$ was found to be about 16 calories per mole of ammonia in the solids, which may be compared with 11 cal/mole, the value found from available data[12] for $AlCl_3 + AlCl_3 \cdot 6\ NH_3$ at about 0° C. A value of $\bar{v}$ was known.

It seems probable that the terms of equation (24) involving p^2 and p^3 may often if not usually be omitted, giving, with elimination of β by equations (20) the relatively simple equation:

$$\log p = \log p_0 - \frac{M(C_p - \bar{c})}{R}\left(\frac{1}{M}\log\frac{T_0}{T} + 1 - \frac{T_0}{T}\right) + \frac{M\lambda_0}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right) + M\left(\frac{\bar{v} - B_0}{RT} + \frac{A_0}{R^2T^2} + \frac{c}{RT^4}\right)(p - p_0) \quad (27)$$

This equation is recommended for solids as the approximation usually next in order to equation (1) with $B = O$. Equation (1) does not appear to have been especially successful and it is but little simpler to apply it to data, when B and C are not known in advance, than equation (27) itself.

5. The Latent Heats of Evaporation.

The latent heat at T_0 in joules or calories will be obtained by multiplying λ_0, obtained as above in say liter-atmospheres (normal), by a factor Q, which may be 101.328 for (absolute) joules, or 24.2122 for 15°-gram-calories.[13]

The latent heat λ at another temperature T is equal to $T(s - \bar{s})$ and may be found by applying the exact thermodynamic equations (28) and (29):

$$s = s_0 + \int_{T_0}^{T} C_p d\ln T - \int_{p_0}^{p} (dv/dT)_p dp \quad (28)$$

$$\bar{s} = \bar{s}_0 + \int_{T_0}^{T} \bar{c}\, d\ln T - \int_{p_0}^{p} (d\bar{v}/dT)_p dp \quad (29)$$

which give the general relation (30):

$$\lambda = \frac{T}{T_0}\lambda_0 + T\int_{T_0}^{T} (C_p - \bar{c})\, d\ln T - T\int_{p_0}^{p} [d(v - \bar{v})/dT]_p dp \quad (30)$$

These integrations are to be performed as in the case of the potentials, that with respect to T being carried out at the pressure p_0, and that with respect to p being carried out at the temperature T.

Assuming that $(C_p - \bar{c})$ and $\bar{v}$ are constant and using the equation of state (19) we obtain the equation

$$\lambda = T\lambda_0/T_0 + \frac{T}{M}(C_p - \bar{c})\log\frac{T}{T_0} - \frac{RT}{M}\log\frac{p}{p_0} - Q\left(\frac{A_0}{RT} + \frac{3c}{T^3}\right)(p - p_0) - Q\left(\frac{B_0b}{2RT} - \frac{A_0a}{R^2T^2} + \frac{2B_0c}{RT^4}\right) \times (p^2 - p_0^2) + \frac{5B_0bc}{3R^2T^5}(p^3 - p_0^3) \quad (31)$$

to accompany equation (24). In the application to the data of Gillespie and Lurie the last two terms of equation (31) were negligible, and the approximate formula:

$$\lambda = T\lambda_0/T_0 + \frac{T}{M}(C_p - \bar{c}) \log \frac{T}{T_0} - \frac{RT}{M} \log \frac{p}{p_0} - Q\left(\frac{A_0}{RT} + \frac{3c}{T^3}\right)(p - p_0) \quad (32)$$

is recommended for use in connection with equation (27). In equations (30) and (31) C_p, $\bar{c}$, and R will be in the same heat units as λ and λ_0, and Q is the conversion factor mentioned above.

6. Controls on Calculations.

The numerical work, the applicability of the simplifying assumptions used and the calculation of the latent heats may be controlled as follows.

Let the vapor pressures be calculated for the experimental temperatures by the equation derived, and designated by p_c. Let the corresponding pressures be calculated by the use of the linear relation (33):

$$\log p = A - C/T \quad (33)$$

and designated by p_l. Let the values of the deviation: dev = $\log p_c - \log p_l$ be plotted against $1/T$. They must lie on a smooth curve, which may now be drawn. Let the slope of the smooth deviation curve at the temperature T be $d\ \mathrm{dev}/d(1/T)$. Then

$$d \log p_c/d(1/T) = d\ \mathrm{dev}/d(1/T) + d \log p_l/d(1/T) = d\ \mathrm{dev}/d(1/T) - C \quad (34)$$

An exact form of the Clapeyron equation is

$$d \log p/d(1/T) = -M\lambda T/[p(v - \bar{v})] \quad (35)$$

The last member of equation (34) should be equal to the right-hand side of (35). The value of this may be found from the value of λ as calculated in pv units and from a value of $(v - \bar{v})$ computed from the equation of state used. This equality may be tested by drawing a line through the point T, p of the deviation plot with the slope calculated from the heat, namely with slope equal to

$$C - M\lambda T/[p(v - \bar{v})];$$

the line so drawn must be tangent to the deviation curve.

A further control is obtained by plotting the deviation: $\log p' - \log p_l$, where p' is the observed pressure, on the same deviation plot. If these points fall on a smooth curve of their own, different from the other smooth curve, the approximations used for smoothing the pressures have been too severe, otherwise not. But if better values of $d\ dev/d(1/T)$ can be thus obtained from the observed points, the value of the latent heat in heat units may be calculated from these values together with the best possible values of $(v - \bar{v})$ from the relation:

$$\lambda = \frac{Qp(v - \bar{v})}{MT}\,[C - d\ \mathrm{dev}/d(1/T)] \tag{36}$$

where C is the same as in equation (33).

7. Summary.

By methods similar to that of Gibbs, general thermodynamic equations have been derived for the vapor pressure and the latent heats. A difficulty is discussed and removed, which appears if we wish to use a partial quantity such as a partial volume for the case of chemical compounds, due to the combination of atoms in definite proportions.

Approximations which may be made when dealing with solid compounds are discussed, and approximate equations are given for the decomposition pressures of solid compounds and their latent heats of decomposition. Methods of applying the equations to experimental data are given, together with a procedure for controlling the accuracy of the calculations.

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